

## The Role of the Charge State of the Molecule and the External Electric Field in the Functioning of Molecular Switches Based on Spiropyran Molecule

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The geometric structure and energy of the electronic system of spiropyran and merocyanine molecules in electrically neutral form, as well as in cationic and anionic form in the presence of an external electric field (from  $-0.02$  a.u. to  $+0.02$  a.u.) were investigated using quantum mechanical methods. Spiropyran and merocyanine molecules with attached hydrogen atom to the oxygen and nitrogen atoms were also studied. It is shown that the attaching of a hydrogen atom to a nitrogen atom causes breaking of N-C<sub>spiro</sub> bond and in the case of attaching to the oxygen C<sub>spiro</sub>-O bond cleavage is observed. In both cases, such cleavage is accompanied by  $sp^3 \rightarrow sp^2$  rehybridization of the atomic orbitals of the spiro atom. It is shown that in the electric field  $E = +0.01$  a.u. the right and left moieties simultaneously turned on  $90^\circ$ , breaking common  $\pi$ -electronic system. It is discovered that in the electric field  $E = +(0.01-0.02)$  a.u. spiropyran molecule with attached hydrogen atom to the oxygen atom transforms into merocyanine molecule.

**Keywords:** Molecular switch, Transformation of molecules in an external electric field, Spiropyran, Merocyanine.

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### 1. INTRODUCTION

Spiropyran (SP) and merocyanine (MC) molecules which transform from one to another under the influence of light are interesting for physicists, chemists and technologists for several decades [1-4]. In the last century, this interest was caused by the development of film materials for optical recording of information (photos on the materials which don't contain silver). The necessity in such investigations has been significantly decreased with the development of computer technology and new technologies for recording photographic images [5]. However, the miniaturization of the elements of hardware has already raised the question of the possibility of using individual molecules as elements of integral circuits. SP-MC molecular system can perform the role of electronic switch successfully since SP molecule is not able to conduct an electric current along the long axis of the molecule, while MC molecule, which has a planar structure and a delocalized  $\pi$ -electron system, has the ability to transfer charged particles along the long axis [6, 7].

Nowadays, the versatility of the SP-MC pair still attracts researchers' attention [8-11]. However, this is a very complicated system, and therefore physical and chemical processes that occur during transformations in this system are still not studied. Attempts to solve the problem by considering shapes of potential surfaces of electronic system in excited states have not been successful yet. Therefore, in this work, authors studied the possibility of interconversions of SP-MC pair in charged states as well as in an external electric field.

### 2. OBJECTS AND METHODS

A pair of molecules that can reversibly transform under the influence of light, has been chosen for research.

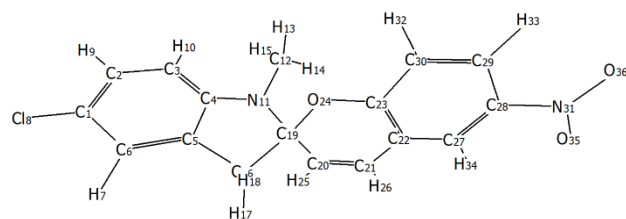


Fig. 1a – General structure of spiropyran molecule

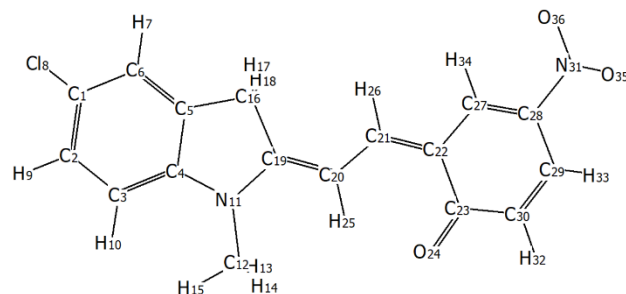


Fig. 1b – General structure of molecule

In this work a quantum-chemical methods of investigation were used due to HyperChem-8 and MOPAC-12 software packages. The MNDO/d [12] and AM1 [13, 14] methods were used to find the geometric structure and the energy structure of the molecules in the ground and excited states.

The charge state of the molecule was set before carrying out calculations. There are three active sites for joining a hydrogen atom or a proton in SP and MC molecules. These sites are nitrogen atom N(11), oxygen atom O(24), which is connected with spiroatom, nitrogen atom N(31) in the nitro group. If it was necessary, hydrogen atom was joined to the oxygen or nitrogen atom before the calculations.

Investigation of the anionic form of the molecules

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requires a particular attention since the energy of affinity to the electron is slight. This leads to the fact that calculated procedure is failing with slight deviations from the real structure of the molecule. Since molecular switches in real conditions functionate with the application of electric field, such investigations were carried out in this work.

### 3. RESULTS AND DISCUSSION

As it can be seen from the geometric structure of the SP molecule (Fig. 1), the oxygen atom O(24), which is a substituent in the phenyl moiety, is attached to the spiroatom of carbon ( $C_{\text{spiro}}$ ). Hence, O(24) closes a six-membered ring. In this case,  $C_{\text{spiro}}$  is characterized by  $sp^3$ -hybridized atomic orbitals. As consequence, we have two independent  $\pi$ -electronic system. Excitation of the SP molecule leads to the cleavage of the  $C_{\text{spiro}}$ -O bond and  $sp^3 \rightarrow sp^2$  rehybridization of atomic orbitals [7, 15]. As a consequence, the MC molecule is obtained. It has a planar structure and extended  $\pi$ -electronic system. If such molecule is placed between electrodes (to achieve this, active substituents are attached at the ends of the long axis of the molecule) and transfer an electron or a hole to the molecule from the electrode, then the charge will be transferred through the molecule to another electrode without any lossless.

In this paper, the mechanisms of the SP-MC conversion in the modified charge state and under the influence of the external electric field were considered.

#### 3.1 Energy of the Electronic System

First of all, the energy of the electronic system of the molecules in various charge states was considered. The results of calculations are given in Table 1.

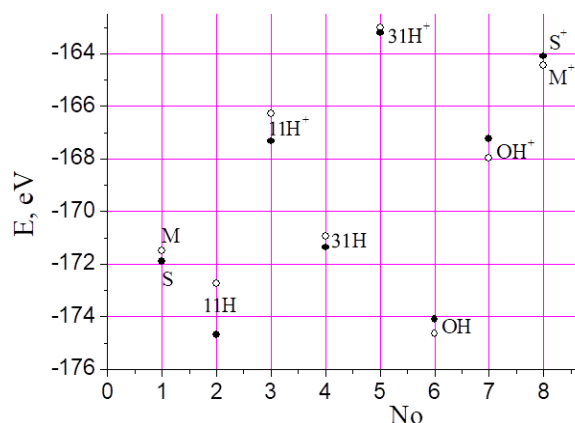
**Table 1** – Energy of electronic system in the ground state of the molecules (neutral and cationic forms)

No	Molecule	$E$ , eV	$E_i$ , eV	Molecule	$E$ , eV	$E_i$ , eV
1	MC	-171,49	7,05	SP	-171,89	7,80
2	MC-11H	-172,73	6,45	SP-11H	-174,68	7,36
3	MC-11H <sup>+</sup>	-166,27		SP-11H <sup>+</sup>	-167,32	
4	MC-31H	-170,92	7,91	SP-31H	-171,35	8,14
5	MC-31H <sup>+</sup>	-163,01		SP-31H <sup>+</sup>	-163,22	
6	MC-OH	-174,65	6,69	SP-OH	-174,09	6,87
7	MC-OH <sup>+</sup>	-167,95		SP-OH <sup>+</sup>	-167,22	
8	MC <sup>+</sup>	-164,44		SP <sup>+</sup>	-164,09	

Obtained results are presented on Fig. 2.

Electronic system of the SP molecule has lower energy MC molecule. As a result, spiropyran is a main form of the studied molecule, but merocyanine can be unstable (when low barrier is present). Molecule's ionization which takes place during carrying out a hole through the molecule stabilizes merocyanine molecule. It's important for the flow of electric current through it. A hole is localized on the highest occupied molecule orbital (HOMO). Values of the ionization energies of the molecules are presented on the Table 1. To ensure the conductivity of

the molecule it's required to transform it from spiropyran form into the merocyanine form. Various variants of joining a hydrogen atom to the studied molecules were considered to find such possibility.



**Fig. 2** – Neutral and cation forms of the spiropyran and merocyanine molecules

Geometric structure with H atom has been achieved by placing it above the target atom (above molecule's plane or molecule's fragment) with subsequent geometric optimization. As can be seen from the Fig. 2 when H atom is connected to N(11) atom the molecule is stabilized and its energy is decreased by 2.8 eV. Therefore, such a reaction will facilitate the return of the merocyanine molecule to spiropyran. To make such an attachment of H atom happened it's necessary that molecular structures in which the binding energy of the H atom is below 2.8 eV are present in the environment. However, switching from spiropyran to merocyanine doesn't occur in this case. Previously unknown effect has been observed: attachment of the H atom leads to break of the N- $C_{\text{spiro}}$  bond. Also,  $sp^3 \rightarrow sp^2$  rehybridization of the spiroatom takes place. But it doesn't expand  $\pi$ -electron system. So, in the new form the molecule can conduct an electric current along the long axis of the molecule.

On the other hand, attaching H atom to N(11) atom in the merocyanine breaks  $\pi$ -electronic system. This leads to terminations of the conductivity of the molecule along the long axis. This effect may be used to build a molecular switch.

Attaching of H atom to N atom in the nitrogroup is energetically unfavorable and doesn't affect on equilibrium between spiropyran and merocyanine molecules.

Attaching of H atom to O atom leads to substantial decreasing of energy of the electronic system of merocyanine molecule which in turn stabilizes it. At the same time, the energy gain from joining the hydrogen atom to the oxygen atom in the SP molecule is less than in the case of N(11). However, attaching of H atom to O atom leads to breaking of the O- $C_{\text{spiro}}$  bond. It may signal as start of switching or as merocyanine stabilization. In both cases of bond breaking  $sp^3 \rightarrow sp^2$  rehybridization takes place. But still there is a question of how to control the switching process which takes place when H atom is attached to O atom.

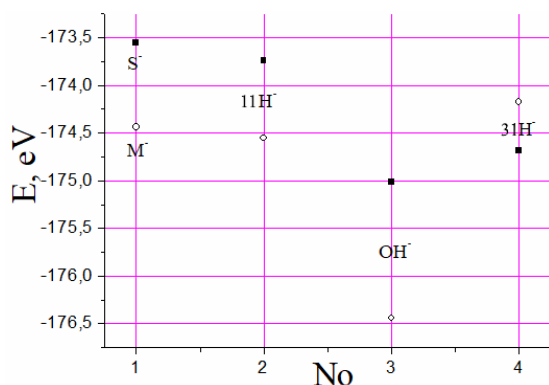
Possibility of electron transfer through the molecules has been studied. Electron can move through the molecule using lowest unoccupied molecular orbital (LUMO).

The results of calculations are presented on Table 2 and Fig. 3.

**Table 2** – Energies of the electronic system of the molecules in anionic form

No	Molecule	$E$ , eV	$E_A$ , eV	Molecule	$E$ , eV	$E_A$ , eV
1	MC-	-174,43	2,94	SP-	-173,55	1,66
2	MC-11H	-174,55	1,82	SP-11H	-173,74	-0,94
3	MC-OH	-176,44	1,79	SP-OH	-175,01	0,92
4	MC-31H	-174,17	3,25	SP-31H	-174,68	3,32

Besides energies of the electronic system in anions of spiropyran and merocyanine, energies of affinity  $E_A$  to electron also are presented. It's notable that affinity of SP-11H is negative. It can be assumed that in this case electron transfer from an electrode to the molecule is unlikely. If molecule is free then such a transfer will be impossible. Additional lowering of energy due to polarization of the nearest environment makes it possible. This negative fact is useful for our system because MC-11H conductivity is absent due to breaking  $\pi$ -electron system.



**Fig. 3** – Energies of the electron system of the spiropyran (•) and merocyanine (◦) in anion form.

From Fig. 3 it can be seen that in the system of SP-MC anions, anion of MC will be energetically beneficial. It can favour not only to the reliability of the flow of electric current, but also to the SP-MC transformation.

For cationic and anionic forms energetically favorable are OH-substituted molecules as for molecules in neutral form. However, in all cases, the addition of a hydrogen atom to the oxygen atom increases (breaks the bond) the Cspiro-O distance. This increase in the anionic form occurs from 1.38 Å to 2.61 Å. Bond order decreases to 0.004, that is, the complete bond cleavage occurs. At the same time, the orthogonality of the moieties in the molecule retains.

### 3.2 Influence of the External Electric Field on the of Spiropyran-Merocyanine System

The external electric field was determined by software and oriented along the long axis of the molecule. Control of the spatial field orientation was carried out with the help of a benzene molecule which took on the role of test. Orientation of the electric field was determined by the distribution of charges on the atoms that forms the benzene molecule. Carrying SP and MC mole-

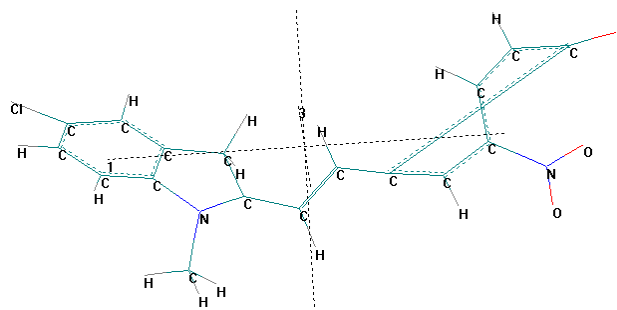
cules in electric field led to the polarization of the molecule and, consequently, to the change in the magnitude of the energy of the molecules' electronic system. Redistribution of charges in the investigated molecules leads to a change in the geometric structure of the molecules. In those cases when it is possible to calculate the energy of an electronic system in molecules with optimized geometry, the results are put down in the Table 3.

**Table 3** – Energies (kcal/mol) of the electronic system of the spiropyran and merocyanine molecules, which were carried in the external electric field

Molecule	Electric field (a.u.)				
	-0,02	-0,01	0	0,01	0,02
Merocyanine	-3987,12	-3952,13		-3994,36	-4075,36
Optimized geometry reactions		-3951,25	-3954,75	-3999,67	-4110,20
Spiropyran	-4013,96	-3979,90		-3965,16	-3983,60
Optimized geometry		-3985,67	-3963,98	-3968,56	-3998,70
MC+	-3822,81	-3778,39	-3776,80	-3824,84	-3947,67
SP+	-3875,85	-3819,53	-3784,12	-3764,43	-3811,60
MC-OH	-4086,64	-4033,02	-4022,91	-4045,07	-4127,27
SP-OH	-4062,47	-4029,38	-4014,71	-4015,28	-4030,61

The value of the negative charge increases on the chlorine atom in those cases when the direction of the electric field has a sign "-". The charge on the chlorine atom reaches "1", and the atom breaks away from the MC molecule in the field  $E = -0.02$  a.u. In addition, in this case the Cspiro-N bond of the molecule is broken. In other cases, the structure of the molecule is remained. In Table 3 it is shown that the placement of the SP molecule in the electric field has changed the magnitude of the energy of the electronic system. This happened due to the polarization and change in the geometry of the molecule.

The investigation of charged molecules, in particular, "MC+" and "SP+" is associated with methodological difficulties, since such molecules in the electric field are continuously moving with both translational and rotational motions. That's why only energies of electronic system of the molecule in the presence of polarization are shown on the Table 3. The investigation of the influence of the electric field on the geometric structure showed that at  $E = -0.01$  a.u. in the cation of MC, the phenyl ring was irreversibly broken off. It was presented on Fig. 4.



**Fig. 4** – Geometric structure of the MC+ in electric field  $E = -0.01$  a.u.

At  $E = +0.01$  a.u. the right and left moieties simultaneously turned on 90°, leaving central ethyl group in the place. Such change in the structure of the molecule actually broke the  $\pi$ -electronic system. However, such struc-



## Роль зарядового стану молекули і зовнішнього електричного поля у функціонуванні молекулярних перемикачів на основі спіропірана

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В роботі проведені дослідження геометричної структури і енергії електронної системи молекул спіропірана і мероціаніна в електронейтральній формі, а також в катіонній та аніонній формі в присутності зовнішнього електричного поля (від  $-0,02$  а.о. до  $+0,02$  а.о.) з використанням квантово-механічних методів. Досліджено також молекули спіропірана і мероціаніна з приєднаним атомом водню до атома азоту або кисню. Показано, що приєднання атома водню до атома азоту викликає розрив зв'язку N-Cspiro, а приєднання до атома кисню - розрив зв'язку O-Cspiro. В обох випадках такий розрив супроводжується  $sp^3 \rightarrow sp^2$  перегибридизацією атомних орбіталей спіроатома. Показано, що в електричному полі  $E = +0,01$  а.о. правий і лівий фрагменти катіона мероціаніна одночасно розгортаються на  $90^\circ$ , розриваючи єдину  $\pi$ -електронну систему. Виявлено, що в електричному полі  $E = +(0,01-0,02)$  а.о. молекула спіропірана з приєднаним до атома кисню атомом водню перетворюється в молекулу мероціаніна.

**Ключові слова:** Молекулярний перемикач, Перетворення молекул в зовнішньому електричному полі, Спіропіран, Мероціанін.

## Роль зарядового состояния молекулы и внешнего электрического поля в функционировании молекулярных переключателей на основе спиропирана

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В работе проведены исследования геометрической структуры и энергии электронной системы молекул спиропирана и мероцианина в электронейтральной форме, а также в катионной и анионной форме в присутствии внешнего электрического поля (от  $-0,02$  а.е. до  $+0,02$  а.е.) с использованием квантово-механических методов. Исследованы также молекулы спиропирана и мероцианина с присоединенным атомом водорода к атому азота или кислорода. Показано, что присоединение атома водорода к атому азота вызывает разрыв связи N-Cspiro, а присоединение к атому кислорода - разрыв связи O-Cspiro. В обоих случаях такой разрыв сопровождается  $sp^3 \rightarrow sp^2$ -перегибридизацией атомных орбиталей спиреоатома. Показано, что в электрическом поле  $E = +0,01$  а.е. правый и левый фрагменты катиона мероцианина одновременно разворачиваются на  $90^\circ$ , разрывая единую  $\pi$ -електронную систему. Обнаружено, что в электрическом поле  $E = +(0,01-0,02)$  а.е. молекула спиропирана с присоединенным к атому кислорода атомом водорода превращается в молекулу мероцианина.

**Ключевые слова:** Молекулярный переключатель, Преобразование молекул во внешнем электрическом поле, Спиропиран, Мероцианин.

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